USING GREEN NANO-PHYTECHNOLOGY FOR REMEDIATION OF WATER POLLUTED WITH FLONICAMID

M.R. Ramadan; Romeh, A. A. and Muhanna, A.H.,
Plant Production Department, Faculty of Technology and Development, Zagazig University, Zagazig, Egypt

ABSTRACT

The preparation of eco-friendly low-cost activated charcoal (Ach), bentonite (Bent), nano zero-valent iron prepared from Marjoram (Mar-nZVI), nano zero-valent iron prepared from Moringa (Mor-nZVI), Mar-nZVI Ach, Mar-nZVI . Bent, Mor-nZVI . Ach, and Mor-nZVI . Bent with and without Plantago major for the removal of flonicamid pesticide from aqueous solution has been investigated. Structure and morphology of Ach, Bent, Mar-nZVI, Mor-nZVI, Mar-nZVI.Ach, Mar-nZVI.Bent, Mor-nZVI.Ach and Mor-nZVI.Bent were characterized by UV spectroscopy, Fourier transform infrared spectroscopy (FTIR), High-resolution transmission electron microscopy (HRTEM), field emission scanning electron microscopy (SEM).

The results showed that, Mar-nZVI Ach, Mar-nZVI .Bent and Ach have faster flonicamid removal at all treatment periods. The percent removal of flonicamid in the water reached 31.81%- 99.42 by Mar-nZVI. Ach, 26.22%-100% by Mar-nZVI . Bent, 28.21%-100% by Ach compared with 1.68%-46.59% in water solution without nZVI or adsorbents between 2hours-8days. Flonicamid was removed more quickly in the presence of Plantago major L. plus nZVI.Ach and Bent than that by P. major alone.

The uptake of P. major roots and translocation of P. major leaves in the water polluted with flonicamid were lower efficient in accumulation of flonicamid from water under the treatments of P. major L. plus nZVI and plus nZVI .Ach and Bent than that by P. major alone.

Conclusively, from these results it be concluded that plantago major L. plus FeNps .Ach and Bent plays a major role for the remediation of flonicamid-contaminated water.

Key words: Flonicamid, green nanotechnology, phytoremediation, water.
INTRODUCTION

Pesticides are chemical intended to control pests and weeds. They are widely used in agricultural fields to protect the crops from pest damages. Among the pesticides find huge applications in the agricultural fields. However, more than 90% of the sprayed pesticides reach the destinations other than their targets because they are sprayed over the entire agricultural field. These chemicals reach the water bodies via agricultural run-offs, direct entry from the spray, industrial effluents, and dust (Khatri and Tyagi, 2015), causing decreases the quality of water (Khatri et al., 2016). Also, Residues of pesticides have significant environmental impacts on aquatic ecosystems and mammals (Joo and Cheng, 2006; Maddah and Hasanzadeh, 2017). Flonicamid (IK1220; N-cyanomethyl-4-trifluoromethylnicotinamide), belongs to the pyridine carboxamide group, is also systemic insecticide with selective activity against aphids and whiteflies that are resistant to other insecticides; the main insecticidal mechanism of flonicamid is starvation due to the inhibition of stylet penetration into plant tissues (Morita et al., 2007). Flonicamid is stable to aqueous photolysis, and is stable/very persistent to aqueous hydrolysis; The water phase DT₅₀ is 33.8 days (stable) and the water-sediment DT₅₀ is 40 days (moderately fast). Flonicamid have water solubility 5,200 mg/L with low partition coefficient (Kₐw 0.263), so its high mobility and very low affinity for soils and sediment (EUFootprint, 2011). Flonicamid offers good persistence in plants, i.e., for about 2–3 weeks (Chawla et al., 2018).

Adsorption is effective method for water cleaning applications. Adsorption has been found to be superior to other techniques for water reuse in terms of initial cost, flexibility, and simplicity of design, ease of operation, and insensitivity to toxic pollutants. This process is a surface phenomenon that depends on the number of sites available, porosity and specific surface area of the adsorbent as well as various types of interactions. (Taghizade et al., 2018)

Nanotechnology is the development and utilization of structures with a size range from 1 nm to about 100 nm where new physical, chemical and biological properties occur such as extremely small size, high surface area to volume ratio, surface modifiability and excellent magnetic properties (Riu et al., 2006). In recent years, zero-valent iron (ZVI) has been widely applied for treatment of contamination because of its easy accessibility, effective degradation of pollutants, generation of very little waste and secondary pollutants (Joo and Cheng, 2006 and Thompson, 2010).

Many researchers have reported the green synthesis of iron nanoparticles using various plant extracts. Biosynthesis of iron nanoparticles (Fe NPs) has been mainly performed using extract of green tea, which is a cheap and local resource. (Hoag et al., 2009). Fe₀/Fe₃O₄ nanoparticles were successfully
synthesised using pomegranate (*Punica granatum*) leaf extract by (Rao *et al.*, 2013). Makarov *et al.*, (2014) reported the synthesis of iron oxide nanoparticles using aqueous extract of *Hordeum vulgare* and *Rumex acetosa*.

Due to high surface area, clay minerals, especially 2:1 smectite type, are well known for their sorption properties. High surface area enables bentonite clay to efficiently scavenge chemical species from wastewater (Dimirkou *et al.*, 2002). Adsorption process by activated carbon is the most efficient and promising fundamental approach in the wastewater treatment processes (Ali and Gupta, 2007 and Gupta *et al.*, 2009).

Therefore, the objective of this study was to investigate the effects of green nanotechnology (iron nanoparticles from medicinal plant extracts, Fe$^0$), Fe$^0$ supported on bentonite and activated charchoal, and Fe$^0$ supported onadsorbents and *Plantago major* for remediation of flonicamid from water.

**MATERIALS AND METHODS**

1. **Pesticide and Plant Material**

Flonicamid 50% W.G., was obtained from the Central Agriculture Pesticide Laboratory, Agriculture Research Center, 7 Nadi EL Said St., Dokki, Giza, Egypt. Broadleaf plantain, *Plantago major* L. seedlings (9–12 cm in height with 4–6 leaves) were collected from Zagazig University, Governorate of Sharkia, Egypt, then transferred to nutrient solution suggested by (Wang, 1986) for one week to acclimation, after that moved to aqueous media, at the rate of one seedling per medium (Romeh and Hendawi, 2017).

2. **Adsorbent Materials used**

Activated charcoal (4-14 mesh) from El Gomhoureya Company, Egypt and bentonite from Sinai Manganese Company, Egypt were used as adsorbent materials. Bentonite was provided primarily as Na-Mt montmorillonite (>90%), the chemical composition was 51.50 % SiO$_2$, 21.50% Al$_2$O$_3$, 1.95% Fe$_2$O$_3$, 1.80% MgO, 0.80% CaO, and 1.80% Na$_2$O, 1.3 % K$_2$O (Abd-El-All *et al.*, 1992). After drying overnight at 80 °C, the raw bentonite was ground and sieved through a 200-mesh screen prior to use in experiments.

3. **Synthesis of nano zero-valent iron (nZVI) and supported nZVI**

The nano zero-valent iron prepared from Marjoram (Mar-nZVI) and Moringa (Mor-nZVI) supported on activated charcoal (Ach), and bentonite (Bent) were prepared according to the method described by (Abbassi *et al.*, 2013).

For the synthesis of Mar-nZVI Ach, Mar-nZVI Bent, Mor-nZVI Ach, and Mor-nZVI Bent, 20 g. of each dry Marjoram (*Origanum majorana* L) and
Moringa (*Moringa oleifera* Lam) leaves powdered were heated up to 80°C in 1L deionized water and filtered using a vacuum filter. A solution of 0.1M FeCl₃ was prepared by dissolving solid FeCl₃ in 1 L of deionized water. This solution was further added into 20g of each bentonite (Bent) and activated charcoal (ACH). Subsequently, each prepared extract was added to the mixture of Bent or Ach and FeCl₃ at a 1:2 ratio (v/v). The resultant mixture was mixed for 1h using a stirrer. After mixing, the mixture was centrifuged at 5000 rpm for 30 min and washed three times with ethylene to remove the residual ferric chloride. The wet paste was then dried in an oven at 60°C overnight, and the final product was grinded before use in the experiment. Mar-nZVI and Mor-nZVI were prepared by a similar procedure as described above without supported material.

4. **Characterization and measurements of zero-valent iron (nZVI) and supported nZVI**

The formation and stability of iron nanoparticles (FeNps) was done by using UV-vis spectrophotometer (Version 530). The absorption spectrum of reaction solutions were recorded at wavelengths ranging from 200 to 500 nm (Narayan and Park 2014).

The morphology, size and shape of F-Fe⁰ were performed by High-resolution transmission electron microscopy (HRTEM), JOEL model JEM-2100 using an accelerating voltage of 200 kV. Sample preparation for TEM analysis involves depositing a drop of aqueous F-Fe⁰ suspension on a carbon-coated copper grid and allowed to dry at room temperature; the transmission electron micrographs is used for recording the particle size and morphology. HRTEM Samples were determined at Al-Azhar University.

The FEI Quanta 250 FEG Scanning electron microscopy (SEM) was used for surface morphological and structural studies of B, B-nZVI, Ach, and Ach-nZVI. Images of various materials were obtained at an operating voltage of 30 kV.

A Fourier-transform infrared spectroscopy (FT-IR) was used to demonstrate the chemical component of adsorbent material and nanoparticles supported on adsorbent material before and after the reaction with flonicamid between 4000–400 cm⁻¹. After sample preparation, mix with potassium Bromide (KBr) for the extent of OH signature.

5. **Experimental design**

The potential of Mar-nZVI and Mor-nZVI supported on two adsorbent materials (Ach and Bent) with and without Plantago major for removing flonicamid from aqueous solution (100 ml) at an initial concentration of 20
mg/L were evaluated. Sixteen treatments were prepared in a randomized design, and each treatment consisted of three replicates as follow: (1) Flonicamid-contaminated water with no plants, (2) Flonicamid-contaminated water with a P. major seedling,

(3-4) Flonicamid-contaminated water amended with 0.2g of Bent and Ach, individually. (5-8) Flonicamid-contaminated water amended with Mar-nZVI and Mor-nZVI separately, with and without a P. major. (9-16) Flonicamid-contaminated water amended with Mar-nZVI ach, Mar-nZVI Bent, Mor-nZVI Ach and Mor-nZVI Bent separately, with and without a P. major.

6. Sample treatment and analysis

After 24 hours, 1, 2, 4 and 8 days post treatment, Plant roots from the water were rinsed in running tap water then blotted, 5 g of leaves, 5 g of roots and 10 ml of water were analyzed for the determination of flonicamid residues by high-performance liquid chromatography (HPLC).

Flonicamid extracted from water using the QuEChERS (Anastasias, 2003) by placing 10 ml of water into a 50 mL polypropylene disposable centrifuge tube, adding 20 mL acetonitrile, vortexing for 1 min followed by addition of 4 g magnesium sulphate, 1 g sodium chloride, 1 g sodium citrate tribasic (SCT) and 0.5 g sodium hydrogen citrate sesquihydrate (SHS) and shaking thoroughly for 1 min. Each sample was then centrifuged for 5 min at 3000 rpm. A 4-mL aliquot of the resulting acetonitrile supernatant was transferred for analysis of flonicamid by HPLC. Fresh root and leaf samples were chopped, mixed well, and then homogenized with dry ice using a high-speed blender. Extraction and cleanup were conducted using QuEChERS method introduced by (Lehotay et al., 2010) and modified as follows: Finely samples (5 g) were weighed into 50 mL Teflon centrifuge tubes; 8 mL of acetonitrile and 2 mL of methanol were added together and the samples were shaken vigorously for 1 min by shaker to ensure the solvent interacted well with the entire samples. The sample tubes were then stored in a refrigerator at −20°C for 20 min. After that, 4 g MgSO_4_ and 1 g NaCl were added and the samples were vortexed immediately for 1 min. The extracts were then centrifuged for 5 min at 5000 rpm. From the upper layer of the prepared sample, 2 mL of the samples were transferred into a 10 mL tube containing 25 mg PSA sorbent, 125 mg MgSO_4_ and the samples were again vortexed for 1 min and then centrifuged for 5 min at 5000 rpm. The obtained residue was finally filtered using a 0.22 μm Nylon syringe filter for HPLC analysis.

The operating parameters were as follows: a C_{18} reversed-phase column was used (250 × 4.0 mm i.e.), mobile phase consisted of 100% acetonitrile with isocratic mode at a flow rate of 0.5 mL/min, and UV detection at 270 nm. The injection volume was 10 μL for quantitative analysis. The retention time of
flonicamid was 2.80 min. The removal efficiency of flonicamid was calculated as follows:

\[
\text{Removal (\%) } = \left( \frac{C_0 - C_e}{C_0} \right) \times 100
\]

where \( C_0 \) and \( C_e \) are the concentration of flonicamid at initial post treatment of each period \( \mu g/ml \), or \( \mu g/g \).

RESULTS AND DISCUSSION

1. Characterization

The surface plasmon resonance (SPR) peaks were recorded at 342nm and 341nm, respectively, for FeNps from Origanum majorana L and Moringa oleifera Lam (Fig. 1), causing the synthesis of FeNps in the size from 2 to 100 nm (Bar et al., 2009; Philip et al., 2011 and Mittal et al., 2013).

![Figure 1](image1.png)

**Figure (1).** UV-visible spectroscopy of iron nanoparticles (FeNps) synthesized with two medicinal plant leaf extracts in 0.1M FeCl\(_3\) solution. (a) Marjoram -FeNps. (b) Moringa - FeNps.
The Scanning Electron Microscopic (SEM) images of adsorbents (ads) and nZVI ads showed the morphology and nanoparticle distribution of nZVI on activated charcoal (ACH) and bentonite (Bent) (Figure 1). The active charcoal have a pore and irregular structure form (Figure 2, A) and when the nanos are added, the shape is taken close to the ring (Figure 2, B, C). The diameters of the nano zero-valent iron prepared from Marjoram supported on activated charcoal (Mar-nZVI ach) were in the range of 37.77 nm – 82.36nm compared with 61.52nm – 91.89nm in nano zero-valent iron prepared from Moringa (Mor-supported on activated charcoal (Mor-nZVI ach) (Fig2,B,C). On the other hand, Bentonite is arranged in the form of sheets (Fig2,D) and when the addition of synthesized nZVI supported on Bent has changed to the shape close to the ring (Figure 2, E, F). The diameters of the nano zero-valent iron prepared from Marjoram supported on bentonite (Mar-nZVI Bent) were in the range of 37.77 nm – 115.3nm compared with 51.32nm – 87.94nm in nano zero-valent iron prepared from Moringa (Mor-supported on bentonite (Mor-nZVI Bent) (Figure 2, E, F). Methods such as scanning electron microscopy (SEM), in view of their ability to directly view the micro-structure of activated carbons have demonstrated enormous potential for use in the study and characterization of activated carbons [Achaw and Afrane, 2008]. Several research studies the role of Ach and Bent for remediation of pollutants from water (Amorim et al., 2013 and Rajak et al., 2018).
Figure (2). Scanning Electron Microscopic (SEM) for nano zero-valent iron supported on Adsorbents. A-C, represents activated charcoal (ACh), nano zero-valent iron prepared from Marjoram supported on activated charcoal (Mar-nZVI Ach) and zero-valent iron prepared from Moringa supported on activated charcoal (Mor-nZVI Ach). D-F represents, bentonite (Bent), nano zero-valent iron prepared from Marjoram supported on bentonite (Mar-nZVI Bent) nano zero-valent iron prepared from Moringa (Mor-supported on bentonite (Mor-nZVI Bent))

The analysis of electron microscopy shows that the formed nanoparticles of nano zero-valent iron prepared from Marjoram (Mar-nZVI), and B, zero-valent iron prepared from Moringa (Mor-nZVI) were circular shapes and sizes. The Mar-nZVI and Mor-nZVI were well separated and there was no agglomeration. The shapes of nanoparticles were circular, with sizes lower than 100nm (Figure 3a, b).

Figure (3). High-resolution transmission electron microscopy (HRTEM). A, nano zero-valent iron prepared from Marjoram (Mar-nZVI), and B, zero-valent iron prepared from Moringa (Mor-nZVI).
**Figure (4).** A Fourier-transform infrared spectroscopy (FT-IR) for adsorbents (Ach and Bent, nano zero-valent iron supported on adsorbents and nano zero-valent iron supported on adsorbents plus flonicamid). (A). Ach (B). Mar-nzvl-Ach (C). flonicamid+Mar-nzvl-Ach (D). Mor-nzvl-Ach (E). flonicamid+Mor-nzvl-Ach (F). Bent (G). Mar-nzvl-Bent (H). flonicamid+Mar-nzvl-Bent (I). Mor-nzvl-Bent (j). flonicamid+Mor-nzvl-Bent
The infrared spectra for Ach and Bent, Mar-nZVI ach, Mar-nZVI Bent, Mor-nZVI Ach, and Mor-nZVI Bent after reaction with flonicamids are shown in Fig. 4. Data in FT-IR spectroscopy (Fig. 4) recorded a broad peak at region 3438 cm$^{-1}$ is assigned to O–H stretching vibration of hydrogen bonded hydroxyl groups (Ahmed and Hameed, 2009 and Valente Nabais et al., 2011). The band at 2924 cm$^{-1}$ denotes the C=C stretching vibrations in alkyne groups, while the peak wavelength at 1630 cm$^{-1}$ is caused by the C=O stretching band of the carboxyl group or alken C=C stretching vibration in aromatic rings (Yang and Qiu, 2010). The absorption peak at 1514 cm$^{-1}$ is recorded to the C–C stretch. The band that appears near 1040 cm$^{-1}$, represents indicates the existence of C–O stretching vibrations in alcohols, phenols, acids, ethers or esters (Figueiredo et al., 1999 and Tongpoothorn et al., 2011). Also, the absorption peak at 873 cm$^{-1}$ is showed to the C–halogen stretches. After loading zero-valent iron prepared from marjoram supported on activated charcoal (Mar-nZVI Ach), there is a shift in the absorption band of 3,438–3,426 cm$^{-1}$, 2,924–2,926 cm$^{-1}$, 1,630–1,646 cm$^{-1}$, 1,514–1,517 cm$^{-1}$, 1,040–1,042 cm$^{-1}$, and 873–865 cm$^{-1}$, while after loading zero-valent iron prepared from moringa supported on ativated charcoal (Mor-nZVI Ach), there is a shift in the absorption band of 3,438–3,440 cm$^{-1}$, 1,630–1,645 cm$^{-1}$, 1,514–1,517 cm$^{-1}$ and 1,040–1,051 cm$^{-1}$. The reaction of flonicamid with Mar-nZVI Ach induced some modifications of the infrared spectra. There is a shift in the absorption band of, 1,514–1,536 cm$^{-1}$ and 873–879 cm$^{-1}$ while the reaction of flonicamid with Mor-nZVI Ach caused shift in the absorption band of 3,438–3,445 cm$^{-1}$, 1,630–1,646 cm$^{-1}$, 1,514–1,517 cm$^{-1}$ and 1,040–1,063 cm$^{-1}$.

The FTIR spectrum specifies the physic-sorption and chemi-sorption of the flonicamid onto the bentonite due to the existence, shift or disappearance of the peaks of functional groups (Fig. 4). FT-IR spectroscopy (Fig. 4)

The bands at 3642 cm$^{-1}$ and 3624 cm$^{-1}$ were assigned to l-Mg-OH stretching and Al-Al-OH stretching respectively. Al-Al-OH bending vibrations band at 916 cm$^{-1}$ and Al-Fe-OH bending vibrations at 795 cm$^{-1}$ were typical of bentonite clays. Consequently, the bentonite utilized in the present study was rich in aluminum and contained a portion of magnesium and iron too (Sikdar et al., 2008). The Si-O stretching band was seen at 1031. The broad peak at region 3426 cm$^{-1}$ was recorded indicates the possible presence of alcohol - O–H, Phenol -OH group, or-NH groups in Bent. The absorption peak at 2929 cm$^{-1}$ is recorded to the C-C-H, C=C-H. Also, observed bands wavelength at 1639 cm$^{-1}$ was assigned to the -OH bending vibrations of water adsorbed in the bentonite (Dutta and Singh 2015 and Shehata et al., 2016). The band that appears near 1034 cm$^{-1}$, represents Si-O stretching band and the absorption peak at 531 cm$^{-1}$ was allotted to the Si-O bending vibration. After loading zero-valent iron
prepared from marjoram supported on bentonite (Mar-nZVI Bent), there is a shift in the absorption band of 3,426–3,439 cm\(^{-1}\), 2,929–2,926 cm\(^{-1}\), 1,639–1,644 cm\(^{-1}\), 1,034–1,039 cm\(^{-1}\), 915–916 cm\(^{-1}\), 690–693 cm\(^{-1}\) and 531–517 cm\(^{-1}\), while after loading zero-valent iron prepared from moringa supported on bentonite (Mor-nZVI Bent), there is a shift in the absorption band of 3,426–3,427 cm\(^{-1}\), 2,929–2,927 cm\(^{-1}\), 1,639–1,643 cm\(^{-1}\), 1,034–1,035 cm\(^{-1}\), 690–692 cm\(^{-1}\) and 531–529 cm\(^{-1}\) and 531–528 cm\(^{-1}\). The reaction of flonicamid with Mar-nZVI bentonite induced some modifications of the infrared spectra. There is a shift in the absorption band of, 3,426–3,439 cm\(^{-1}\), 2,929–2,926, 915–916 cm\(^{-1}\), 690–694 cm\(^{-1}\), and 531–521 cm\(^{-1}\). while the reaction of flonicamid with Mor-nZVI Bent caused shift in the absorption band of 2,929–2,930 cm\(^{-1}\), 1,639–1,644 cm\(^{-1}\), 1,034–1,035 cm\(^{-1}\), 792–791 cm\(^{-1}\), 690–693 cm\(^{-1}\) and 531–528 cm\(^{-1}\) and 531–528 cm\(^{-1}\).

2. Remediation of water polluted by floncamid by nZVI supported on adsorbents

The preparation of eco-friendly low-cost activated charcoal (Ach), bentonite (Bent), nano zero-valent iron prepared from Marjoram (Mar-nZVI), nano zero-valent iron prepared from Moringa (Mor-nZVI), Mar-nZVI supported on Ach, Mar-nZVI supported on Bent, Mor-nZVI supported on Ach, and Mor-nZVI supported on Bent with and without Plantago major for the removal of flonicamid pesticide from aqueous solution has been investigated in Figures 5 and 6.

The results showed that Mar-nZVI supported on Ach, Mar-nZVI supported on Bent and Ach have faster floncamid removal at all treatment periods, this attributed to the adsorptive capacity of Ach and presence of the adsorbents, Ach and Bent in the composite have served in decreasing the aggregation of the nZVI chains and thereby resulted in higher surface activity of the nanoparticles, and therefore faster flonicamid removal (Shi et al., 2011; Wang et al., 2013 and Reyes et al., 2014). The percent removal of flonicamid in the water reached 31.81%–99.42 by Mar-nZVI supported on Ach, 26.22%–100% by Mar-nZVI supported on Bent, and 28.21%–100% by Ach compared with 1.68%–46.59% in water solution without nZVI or adsorbents between 2hours–8days (Figure 6). Studies have shown that many pesticides can be destroyed using ZVI. It also has been successfully used in dechlorination of highly recalcitrant pesticides and herbicides (Doong and Lai, 2006 and Sayles et al., 1997). When halogenated organic pollutants are treated with ZVI, oxidation of ZVI and Fe(II) provides electrons for dechlorination (Satapanajaru et al., 2008). Young-Soo et al., (2003) studied the reduction of eleven nitroaromatic pesticides with zero-valent iron powder. Shi et al., (2011) tested nanoparticles
Figure (5). Degradation of flonicamid in water by zero-valent iron nanoparticles supported on different adsorbent materials (nZVI ads).
Figure (6). Percent removal of flonicamid in water by zero-valent iron nanoparticles supported on different adsorbent materials (nZVI ads).

zero-valent iron (nZVI), and iron nanoparticles zero valence on a matrix of bentonite (B-nZVI), in the removal of Cr (VI) in water and soil solution contaminated with this metal. The removal of other pollutants such as chlorinated organic compounds, pesticides, phenols, amines, and organic acids through such nanoparticles has been studied (Wang et al., 2013). Polymer-clay nanocomposites have received a great deal of attention, including studies on developing the composites as sorbents for nonionic and anionic pollutants (Churchman, 2002), organic pollutants (Breen, 1999), anionic herbicide (Radian and Mishael, 2008), and atrazine (Zadaka et al., 2009).
Ach is good potential to remove various types of pesticides. The adsorption capacity of pollutants by Ach may involve one or more mechanisms, such as hydrophobic effect, covalent bonding, π-π interactions, hydrogen bonding, and electrostatic interactions (Yang and Xing, 2010 and Pyrzynska, 2011). Adsorption may also take place through hydrogen bonding between functional groups such as -COOH, -OH, -NH2 and organic molecules (LUQUEÑO et al., 2017). Salman et al., (2011) showed that, The banana stalk activated carbon (BSAC) is an efficient adsorbent for the adsorptive removal of 2,4-D and bentazon from aqueous solutions. (BSAC) was characterized by Fourier transform. Infrared spectroscopy (FT-IR) analysis. The adsorption of several organic contaminants in water such as pesticides, phenols, and chlorophenols has been reported recently in the literature (Sanchez Camazano and Sanchez Martin, 1983; Ainsworth et al., 1987; Rodriguez et al., 1988; Shu et al., 1997; Torrents and Jayasundera, 1997; Danis et al., 1998 and Konstantinou et al., 2000).

3. Nano-Phytotechnological removal of flonicamid polluted water

Data in Table 1 and Figure 7 showed that flonicamid was removed more quickly in the presence of Plantago major L. plus nZVI and plus nZVI supported on Ach and Bent than that by P. major alone (Table 1). The results indicate that, flonicamid removal efficiency by each nZVI, nZVI supported on adsorbent, nZVI plus P. major and nZVI supported on adsorbent plus P. major were nearly 100% (Figure 7).

The uptake of P. major roots and translocation of P. major leaves in the water polluted with flonicamid were lower efficient in accumulation of flonicamid from water under the treatments of P. major L. plus nZVI and plus nZVI supported on Ach and Bent than that by P. major alone. This is attributed to the role nZVI alone or combined with adsorbents in degradation of flonicamid in water, therefore the concentration of flonicamid was more decreased in the roots and in the leaves of P. major (Table 1). Pillai and Kottekottil, (2016) show that the removal of endosulfan reached 82% was removed within 7 days when nano phytoremediation experiments were conducted with A. calcarata then gradually decreased, probably due to the activity of nZVI decreased over time. In addition, removal efficiency was found to be highest when nano-phytoremediation experiments were conducted in soil with the TNT/nZVI ratio of 1/10 with the complete TNT remediation (initial TNT concentration: 100 mg/kg) within 60 days (Jiamjitrpanich et al., 2013).
Table 1. Degradation of flonicamid in water by zero-valent iron nanoparticles supported on different adsorbent materials (nZVI ads) plus *P. major*.

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Days after treatments</th>
<th>2h (µg/g)</th>
<th>1 day (µg/g)</th>
<th>2 days (µg/g)</th>
<th>4 days (µg/g)</th>
<th>8 days (µg/g)</th>
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<tr>
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<td>12.44</td>
<td>10.92</td>
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<td>13.82</td>
<td>10.01</td>
<td>7.90</td>
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<td>6.92</td>
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<tr>
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<td>8.01</td>
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<td>8.07</td>
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Figure (7). Percent removal of flonicamid in water by zero-valent iron nanoparticles supported on different adsorbent materials (nZVI ads) plus *P. major*.
Conclusively, from these results it be concluded that plantago major L. plus FeNps Ach and Bent plays a major role for the remediation of flonicamid-contaminated water.

REFERENCES


Validation, residue analysis, and risk assessment of fipronil and flonicamid in cotton (Gossypium sp.) samples and soil. Environmental Science and Pollution Research 25:19167–19178.


Morita, M., T Ueda, T. Yoneda, T. Koyanagi and T. Haga(2007) Flonicamid, a novel insecticide with a rapid inhibitory effect on aphid feeding Ishihara Sangyo Kaisha, Ltd, Central Research Institute, 2-3-1 Nishi-shibukawa, Kusatsu, Shiga 525-0025, Japan


The use of nanotechnology in the treatment and cleaning of water is a comprehensive and holistic approach. The treatment of water by metallic nanoparticles in the field of nanotechnology is one of the key technologies in the field of water treatment. The treatment of water by metallic nanoparticles is based on the principle of the Polanyi theory, which is used to describe the adsorption of organic compounds by carbon nanomaterials in aqueous phase. The treatment of water by metallic nanoparticles is an effective method to reduce the concentration of nitroaromatic pesticides and the removal of atrazine from water by polycation-clay composites.

Este estudio utiliza la nanotecnología para el tratamiento de agua e incluye la purificación de agua y la remoción de compuestos orgánicos. Se utiliza la teoría Polanyi para describir el adsorción de compuestos orgánicos por materiales de carbono en fase acuosa. Se compara el tratamiento de agua con nanopartículas metálicas y el tratamiento con carbón activado.

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